



Boron as a promoter in the goethite (α -FeOOH) phase: Organic compound degradation by Fenton reaction



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ABSTRACT

The aim of this study was to obtain iron oxides (goethite phase, α -FeOOH) to be used as Fenton catalysts in the catalytic oxidation of methylene blue (MB). Moreover surface modifications were attempted by treating the oxides with boric acid in order to improve the materials' catalytic properties through the generation of more active groups on the surface of goethite. The types of structures formed on the surface were investigated through the following characterization techniques: vibrational infrared spectroscopy, Mössbauer spectroscopy, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy and BET surface area measurements. The results of these characterization analyses showed complexation of boric acid on the surface of goethites and the partial reduction of some Fe(III) to Fe(II) species, resulting of a hybrid material containing both goethite and magnetite phases. When tested in the oxidation of organic compounds, the new class of iron oxide showed high capacity for degradation of organic compounds present in the solution. The Gt-B catalyst exhibited enhanced catalytic activity in degradation of methylene blue compared with the pure goethite, especially Gt-B₁ × 4 which, after 240 min of reaction, was able to degrade about 80% of the MB in solution. The increase in the catalytic activity was assigned to the role of boron as a promoter in the transfer of electrons from iron to hydrogen peroxide, the increasing of surface area and the presence of Fe(II) species, which are kinetically more favourable for the Fenton's reaction. In addition, theoretical calculations were carried out at the density functional theory (DFT) level in order to investigate the interaction between goethite and boric acid. The theoretical findings showed that the treatment with the H₃BO₃ significantly modifies the electron density of goethite (100).

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1. Introduction

Many organic compounds are considered potential contaminants in natural waters because of their high toxicity, difficult natural degradation and, therefore, high persistence in the environment [1–3]. The removal or destruction of organic contaminants in effluents has always been a serious problem for the productive sector. Thus, several studies have been conducted aiming to find new methods to minimize the impacts [4–6].

The intensive search for processes to control environmental pollution leads to optimization studies of advanced oxidation processes (AOPs). These processes degrade the recalcitrant organic pollutants in the environment, yielding final much harmless products such as carbon dioxide, water and salts. For these processes,

the degradation is mainly due to the formation of hydroxyl radicals (OH•), which are highly reactive species.

In the case of the Fenton-like reaction, in which radicals are generated by the decomposition of hydrogen peroxide on the surface of an heterogeneous iron phase, the formation of these radicals depends on the electron transfer capability from the metal to hydrogen peroxide [7]. So, it is interesting for the catalyst to be characterized by the ease of changing the oxidation state of their cations. In this context, the use of a mixed valence compound (Fe(III)/Fe(II)) with the capacity of not only donating but also receiving electrons is very suitable for this type of redox reaction [8].

Literature describes well the potential of iron oxide based minerals to catalyze the oxidation of organic compounds by Fenton and Fenton-like reactions [3,9–12]. Goethite (α -FeOOH), a stable iron oxyhydroxide, usually displays a strong affinity for oxyanions. Such affinity has a significant impact on the physical and chemical properties of goethite, which can, after interaction, lead to a different material from the precursor oxide [13]. This possible modification becomes quite interesting, since, in heterogeneous catalysis, the method of preparing a catalyst determinates its catalytic activity

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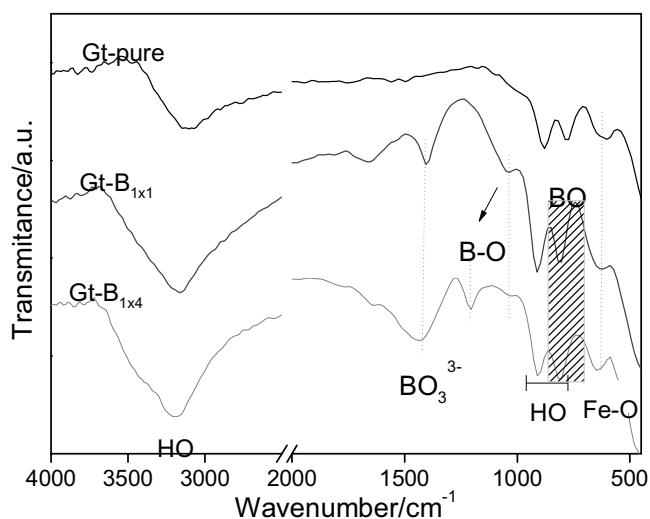


Fig. 1. FTIR spectra for Gt-pure, Gt-B₁ × 1 and Gt-B₁ × 4 samples, recorded at RT.

and selectivity. In this context, modification methods are being increasingly studied for the optimization of these properties.

The modification of goethites was first performed based on the behavior of their analogues, such as AlOOH, and natural systems containing replacing elements. A typical case of natural doping occurs with aluminium goethites, systems in which approximately 30% substitution has been observed [14]. Also in the natural environment it has been found that a significant fraction of boron is presented bound to the surfaces of iron minerals and these composites exhibit properties different from pure materials' properties. Thus, there is an interest on methods for the preparation transition metals and boron compounds, especially in the form of particles for technological and environmental applications [15,16]. Routes of synthesis using sodium borohydride (NaBH₄) and boric acid (H₃BO₃) are well diffused in the literature. However, the reduction of metal ions caused by treatment with NaBH₄ modifies the structure of the material and generally can change desirable characteristics of the catalyst and the specific surface area [17,18].

Studies on boric acid modified goethites showed promising results for photocatalytic degradation of organic compounds [19–21]. These studies showed an increase in the oxidation rate and assigned it to the facilitation in the electron transfer process created by the formation of surface complexes, in addition to the greater separation in the electron-gap pair, which makes it impossible for pure goethites to be used in photocatalytic processes. However, the way boron complexes with iron oxides, the electron-gap separation mechanism for the photoassisted processes and the possibility of reducing some Fe(III) species have not been fully elucidated [20,22,23], as well as the activity of boron-modified goethites on unirradiated processes, which are limited to metal adsorption processes.

Given the above shown considerations, this study was conducted with the general aim of better understanding the structure and catalytic properties of a series of synthetic boron-modified goethites. This material was applied in Fenton systems for the degradation of organic compounds of environmental concern. In order to achieve this goal, the following theoretical and experimental strategy were followed: (i) synthesis of a series of iron oxides in the goethite phase; (ii) modification of the surface of the synthesized materials by the impregnation of boron (iii) characterization and catalytic activity testing for the materials in the oxidation of methylene blue using boron-modified goethite/hydrogen peroxide (Fenton-like reactions) (iv) performing of DFT level theoretical calculations.

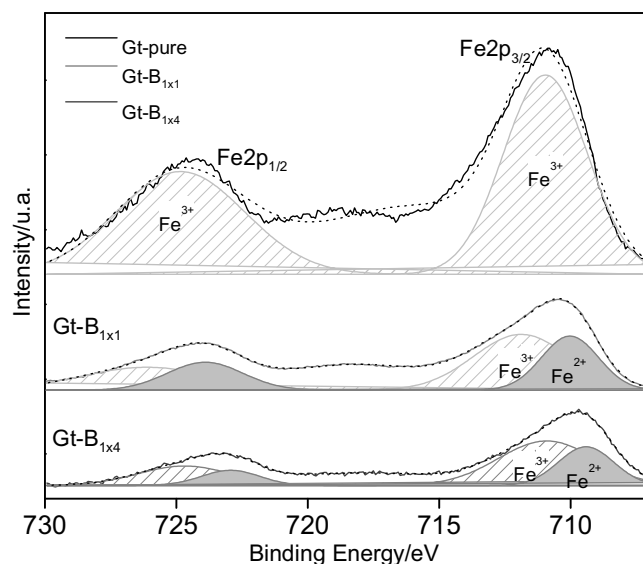


Fig. 2. Excited photoelectron spectroscopy by X-ray in the iron 2p region.

2. Experimental section

2.1. Preparation of the materials

The precursor used in this study was the synthetic goethite prepared using the method described by Schwertmann and Cornell (2003) [14] which consists of dropwise addition of 90 mL of 5 mol L⁻¹ NaOH into a 0.1 mol L⁻¹ Fe (NO₃)₃·9H₂O solution. The resulting suspension was hydrothermally treated at 60 °C for 72 h. After this time, the material was washed with distilled water at room temperature until neutral pH. Then is filtered and dried at 60 °C for 24 h. These samples are henceforward denoted the Gt-pure. Compounds of the α-FeOOH-B type (Gt-B) were synthesized by the reaction of goethite particles with H₃BO₃. Mixtures consisting of two different weight proportions of iron oxide and H₃BO₃ were used (1:1 and 1:4 wt:wt). The suspensions were obtained by the addition of 1 g of goethite to 50 mL of distilled water under magnetic stirring. To the suspension, 100 mL of a 0.2 mol L⁻¹ HCl solution was added drop-wise, Then 50 mL of the H₃BO₃ solution (1:1 and 1:4 wt:wt), and kept stirring for 30 min. After this time, the materials was washed repeatedly with distilled water at room temperature until neutral pH and then was filtered and dried at 60 °C for 24 h. These samples are henceforward denoted the Gt-B₁ × 1, Gt-B₁ × 4, respectively.

2.2. Characterization of the materials

The Brunauer–Emmett–Teller (BET) area were determined through nitrogen adsorption at 77 K (Micromeritics ASAP 2000). The Fourier transform infrared (FTIR) spectra were obtained in a Digilab Excalibur spectrometer, FTS 3000 series, 400 cm⁻¹ to 4000 cm⁻¹ spectral range and 4 cm⁻¹ resolution. FTIR spectra were measured on KBr pellets prepared by pressing mixtures of 1 mg dry powered sample and 100 mg spectrometry-grade KBr under vacuum, with precaution taken to avoid moisture uptake. The X-ray photoelectron spectroscopy (XPS) analyses were performed using a spectrometer of Kratos Analytical, model XSAM HS. Exciter source was employed radiation Kα-Mg. As binding energy reference, 284.6 eV was used for the C1s signal of hydrocarbon (C–C or C–H). Mössbauer spectroscopy was used to study the distribution of the iron phases in the material. The samples were diluted and triturated with sucrose to obtain 10 mg cm⁻² of iron. The Mössbauer spectra were obtained at room temperature, using a

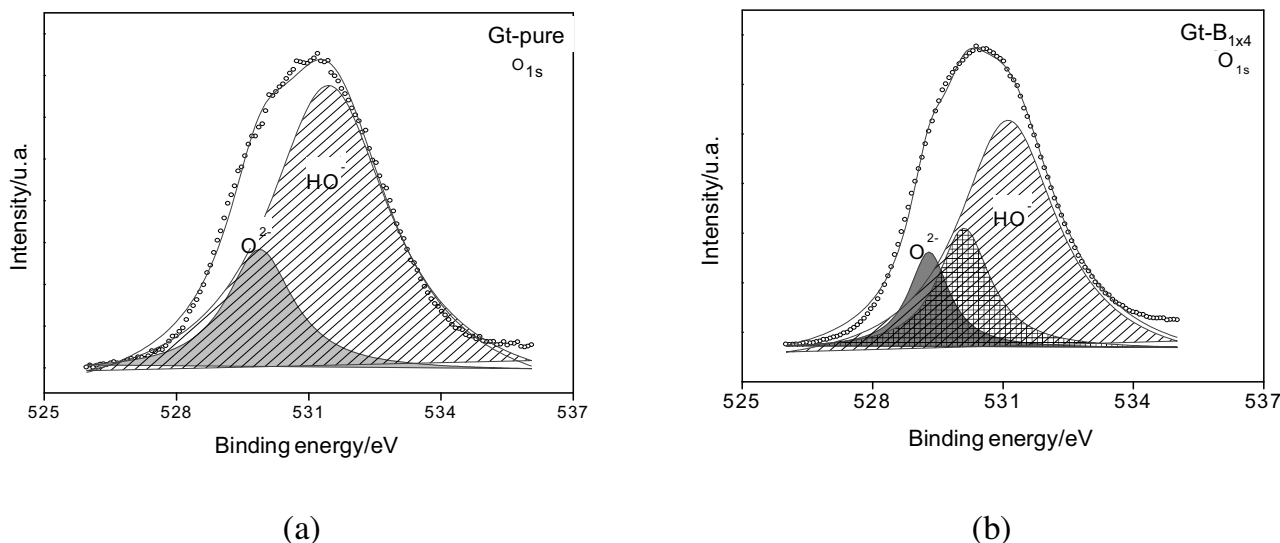


Fig. 3. X-Ray Photoelectron Spectroscopy in the oxygen 1s region for (a) Gt-pure (b) Gt-B₁ × 4.

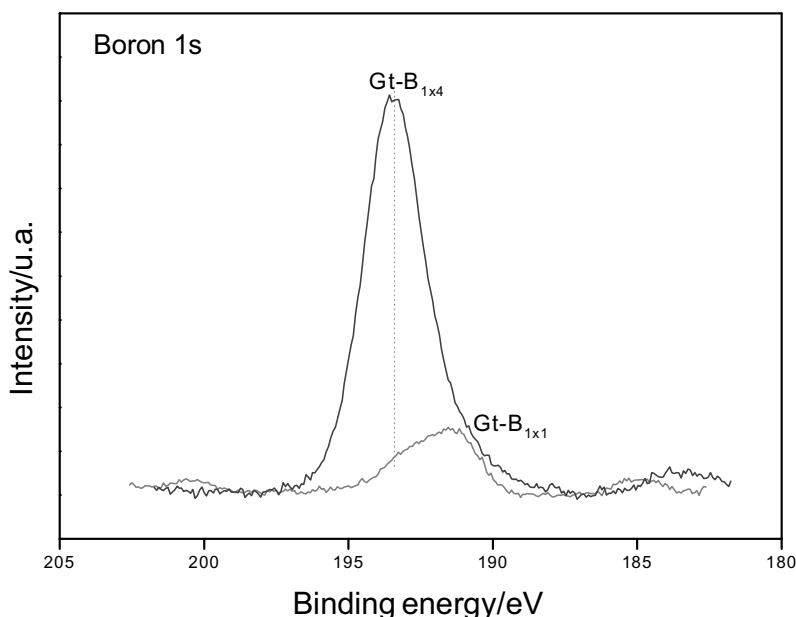


Fig. 4. X-Ray photoelectron spectroscopy in the boron 1s region.

spectrometer with transducer and CMTE model MA250 function generator, and a $^{57}\text{Co}/\text{Rh}$ source. The samples were prepared in pellets, used as absorbers. The isomeric displacement of the samples was referenced by calibration using a metallic iron leaf ($\alpha\text{-Fe}$). The X-ray absorption spectra were acquired on the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil) with K using synchrotron radiation iron with at least three spectra collected for each sample. The LNLS operates at 1.37 GeV and 250 mA. The energies were achieved with silicon crystal monochromators with energy 7112 eV for system calibration.

2.3. Catalytic tests

In a typical test, the catalytic activity for methylene blue degradation was evaluated in a reaction carried out in amber vials, magnetically stirred at 100 rpm, reaction time of 30, 60, 120, 180 and 240 min. For each run were used 10 mg of catalyst (powder), 9.9 mL of 50 mg L^{-1} methylene blue solution and 0.1 mL of

H_2O_2 (50% V/V), added at the beginning of the reaction, with the $[\text{MB}]:[\text{H}_2\text{O}_2]=9.5\cdot 10^{-3}$ [24,25]. All reactions were carried out at room temperature (25°C). The pH for the catalytic tests was the natural pH of the methylene blue solution (6.0 ± 0.5) along the reaction. At this pH, no discoloration is observed in the absence of catalyst. Methylene blue adsorption test was performed under the same conditions but in the absence of oxidant. Each run was centrifuged (15 min at 10000 rpm), and an aliquot of the supernatant was analyzed by UV–vis measurements (Shimadzu-UV-1601 PC) on $\lambda=665\text{ nm}$, and by electrospray ionization mass spectrometry (Agilent-1100 MS-ion trap), allowing the identification of possible intermediate compounds formed during the oxidation of MB. The sample was inserted into the apparatus by infusion at a rate of $5\text{ }\mu\text{L min}^{-1}$, with load control in the quadrupole set to 30 000 and positive way. The drying gas temperature (N_2) was 325°C and the flow rate was 4 L min^{-1} , with extraction potential of -3.5 kV ions. To evaluate whether there was leaching of the active species, the supernatant of the catalytic test using Gt-B₁ × 4 material was

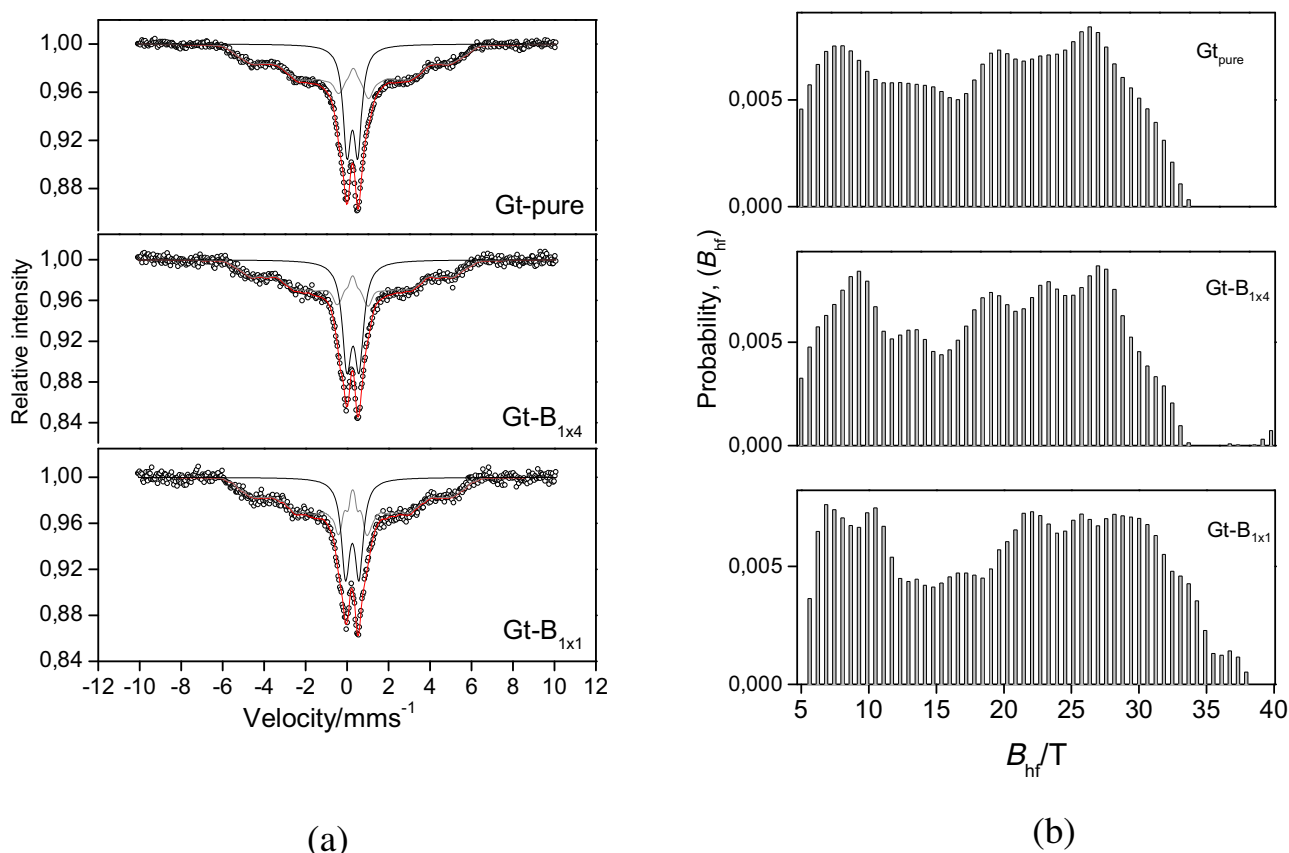


Fig. 5. Mössbauer spectra for samples of pure goethite, Gt-B₁ × 1 and Gt-B₁ × 4, obtained at room temperature (25 °C) and distribution of hyperfine fields for samples (b).

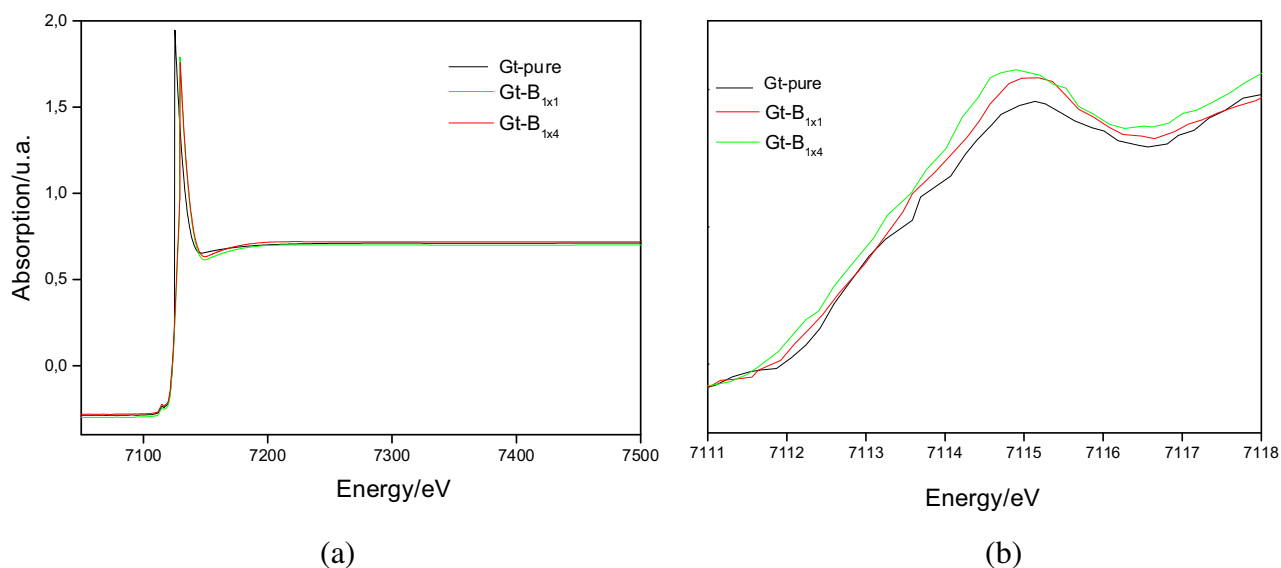


Fig. 6. XANES studies for the materials: (a) XANES spectra, XANES with the extended pre-edge region (b).

recovered by filtration (0.22 μm membrane). Then 9.8 mL of the supernatant, 0.1 mL of the 500 mgL^{-1} methylene blue solution (final concentration of 50 mgL^{-1}) and new portion 0.1 mL of H_2O_2 50% were mixed. The reaction was monitored as described above, using UV–vis spectrophotometric measurements. To evaluate the stability of the catalyst, Gt-B₁ × 4 was re-used in a sequential runs under the same conditions, 4 h for each run, the supernatant analyzed by spectrophotometric measurements, and a new load of MB

and oxidant in the same concentrations were added. This procedure was repeated up to 15 runs.

2.4. Computational methods

For the construction of the cluster crystallographic data obtained from experimental studies were used. The crystal data were $a = 9.950 \text{ \AA}$; $b = 3.010 \text{ \AA}$; $c = 4.620 \text{ \AA}$, in space group Pnma , with

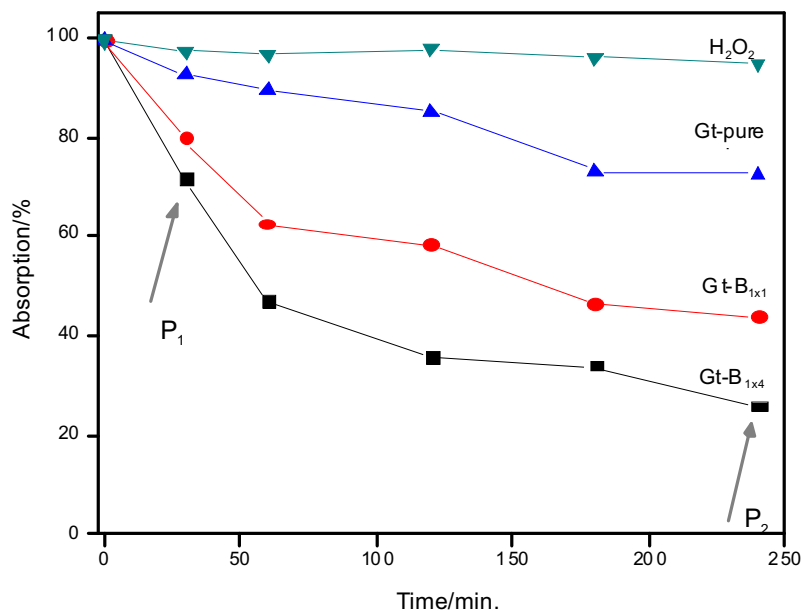


Fig. 7. Methylene blue dye oxidation kinetics in the presence of H_2O_2 and catalyst. The arrows indicate the points P1 and P2, referring to time intervals that were also monitored by ESI-MS.

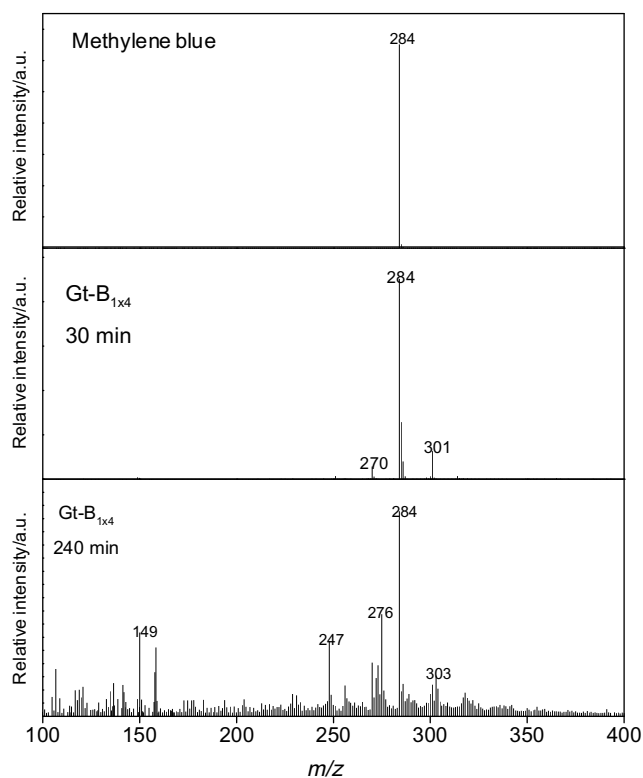


Fig. 8. Mass spectra obtained by electrospray ionization and mass analyzer ion trap type used for monitoring the oxidation of MB by $\text{Gt-B}_{1 \times 4}$ catalyst in points P1 (a) e P2 (b).

the following coordinates for the atoms of Fe: $x=0.145$, $y=0.250$, $z=-0.045$; H: $x=-0.080$, $y=0.250$, $z=-0.380$; O1: $x=-0.199$, $y=0.250$, $z=0.288$ and O2: $x=-0.053$, $y=0.250$, $z=-0.198$ [1]. The calculations in periodic conditions were performed by using the package ADF-BAND 2012.01 (Amsterdam Density Functional). This program calculates the electronic structure of periodic systems in one, two or three dimensions within the density functional theory (DFT). An important feature of this program is that it performs

numerical integrations for all the matrix elements. The integration accuracy in real space and the sampling of the Brillouin zone for the integration accuracy in k-space are the two major numerical parameters in the calculation. In that sense, each face of goethite ($\alpha\text{-FeOOH}$) (100, 010, 110 101, 011, 001), was totally optimized by periodic density functional theory calculations employing generalized gradient (GGA) corrections, self-consistently included through the Perdew-Becke-Ernzerhof (PBE) formula. A triple-z Slater-type (TZP) basis set was used for Fe, B, O and H atoms. The potential energy surface calculations between boric acid (H_3BO_3) and some faces of goethite were performed with the functional PBE and basis set TZP.

3. Results and discussion

3.1. Characterization of the materials

3.1.1. Infrared vibrational spectroscopy (ftir)

Fig. 1 shows the FTIR spectra for the pure goethite and Gt-B samples. Gt-pure FTIR spectrum corresponds to a pure $\alpha\text{-FeOOH}$ sample [4,11]. The spectra of the materials are very similar, characterized by the bands located near 3230 cm^{-1} , which have been attributed to the bulk OH stretch. Intense OH bending bands located at 880 and 780 cm^{-1} correspond to in and out of the plane (100) vibrations and are important in the diagnosis of goethite phase [14]. The bands at lower wave numbers (640 cm^{-1}) correspond to Fe–O and Fe–O–H stretching vibrations or lattice vibration bands.

From the infrared spectra of the Gt-B materials some strong IR absorption bands can be noticed at 1136 (symmetric stretch B–O) and 1208 cm^{-1} (asymmetric stretch B–O) and agree well with those of BO_3^{3-} and $\text{B}(\text{OH})_3$ boron groups [26,27]. There are two broad peaks near 750 and 780 cm^{-1} that arise from the out of the plane B–OH bending vibration, and these vibrations overlap with some of the other B–O stretching vibrations and also with the goethite phase bands. The bands located at 1421 cm^{-1} can be assigned to the asymmetric B–O stretching vibration. The strong IR absorption band at 3230 cm^{-1} can be attributed to OH vibration [26]. From the above shown analysis, it can be said that boron was incorporated in the surface of the iron oxide.

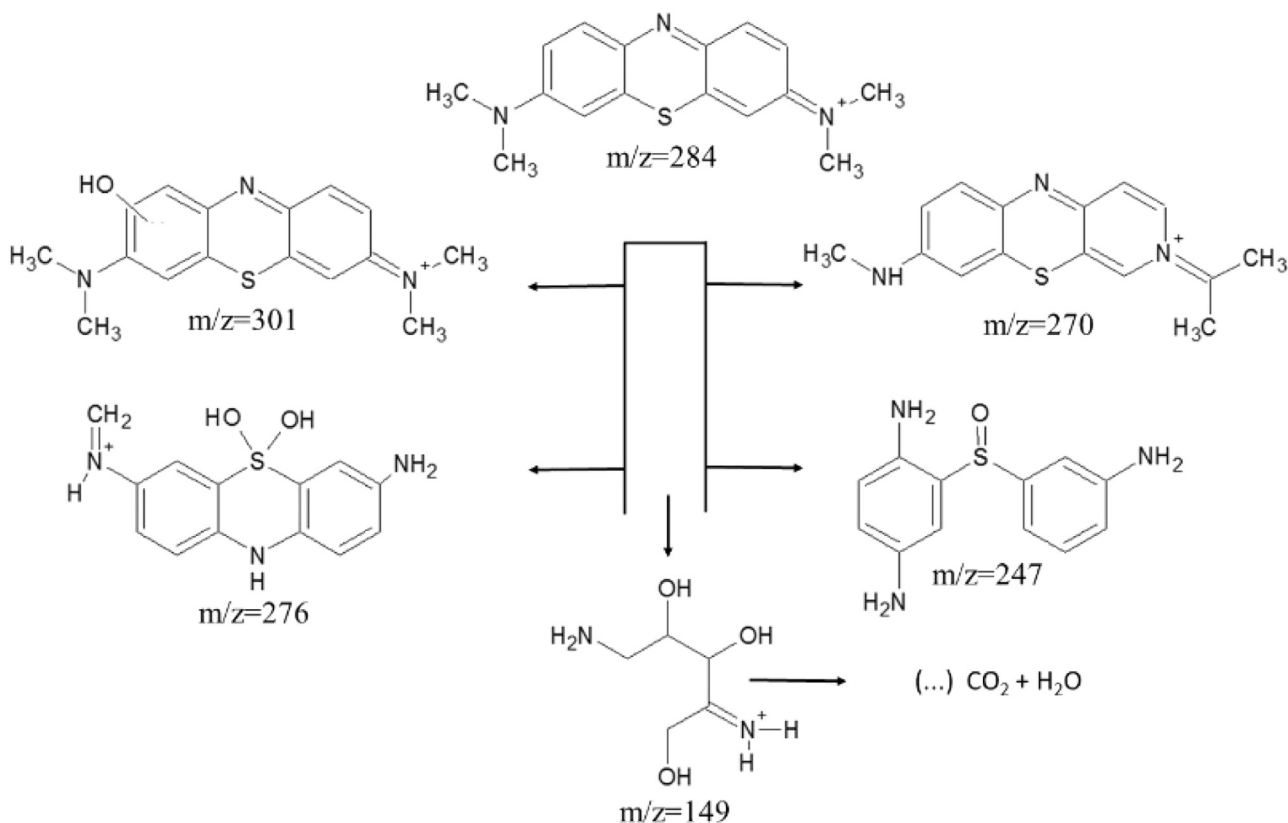


Fig. 9. Possible intermediates formed in the methylene blue oxidation.

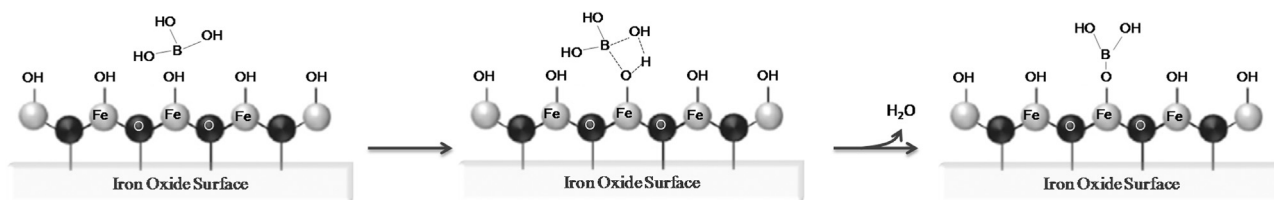


Fig. 10. Surface reaction of goethite with boric acid (H_3BO_3).

Regarding the data obtained by FTIR for the region between 500 and 1000 cm^{-1} , it is interesting that a band related to Fe–OH vibration and a second one related to B–O vibration coincide in 790 cm^{-1} . For pure goethite, the band related to the vibration at 890 cm^{-1} is greater than that at 790 cm^{-1} . However, for the Gt- $\text{B}_1 \times 4$ material, a reversal behaviour can be noticed, with the bands at higher wavelengths corresponding to slightly lower relative intensities. This behavior is directly related to the fact that in this material (Gt- $\text{B}_1 \times 4$), the greatest amount of boron already provides the coupling of the two bands (Fe–OH and B–O) in regions near 790 cm^{-1} , which causes overlapping and changes in the relative intensities of those two signals [27]. This change in the goethites absorption profile is due to the change of the Fe–OH-surface for Fe- $\text{BO}_2(\text{OH})_2$ -surface, what once again proves the impregnation of boric acid on the surface of the material.

3.1.2. X-ray photoelectron spectroscopy (xps)

XPS measurements of pure goethite and Gt- $\text{B}_1 \times 4$ samples were analyzed on the Fe2p, O1s e B1s regions. The spectra on the Fe2p region for the materials are shown in Fig. 2.

The energy values found from the XPS spectrum for Gt-pure material for both iron 2p_{1/2} and iron 2p_{3/2} are typical values of goethite phase Fe(III), these values have been reported in the

literature as 711 and 724.5 eV , respectively [22]. When the results shown in Fig. 2 are analyzed for the boron-containing materials, one can see a distinct spectrum if compared to Gt-pure spectrum. The signs were broad and shifted to a lower binding energy, for Gt- $\text{B}_1 \times 4$ this energy difference exceeds 1 eV , suggesting there by that the boron addition process may have caused a change in iron's chemical environment. Through Gaussian deconvolution analysis of those signals it was observed that the extension allows these delocalized signals to be decomposed into two different ones with varying intensities. Iron oxides such as magnetite (Fe_3O_4) have lower binding energy signals. Thus, the change of the XPS spectrum suggests that boron may contribute to the goethite's surface dehydroxylation due to the appearance of new locations of the type Fe–O–B, especially because the chemical shifts are due only to the surface's first layer. Thus, the disorder caused by the addition of the acid can be related to this surface dehydroxylation, which in turn can lead to the reduction of some Fe(III) species. The iron species present on the surface of the catalyst play an important role in Fenton system mechanisms, in which reactions employing Fe(II) species are more favourable than Fe(III).

The Gaussian deconvolution analysis of Gt-pure in the oxygen region is presented on Fig. 3, where (a) indicates that the spectrum may be divided into two signals with different intensities.

Different signals were not identified for the pure sample. The first band at 531.3 eV can be attributed to the HO[−] group and the smaller one in 528.9 eV occurs due to the Fe–O bonds, probably corresponding to O₂[−] in the iron oxide structure [28]. These are typical features of an orthorhombic goethite structure, which can be best understood as Fe(III) ions surrounded by three oxygen atoms and three hydroxyl groups, giving rise to the octahedral structure FeO₃(OH)₃, which forms double chains sharing edges that bind themselves to the other chains through apexes sharing and hydrogen bonding. On the other hand, the Gt-B_{1 × 4} spectrum was split into three peaks of different intensities and energy. Those peaks show that boron is in a kind of molecular interaction B–O, B–OH and a third type which has not yet been identified, these interactions are presented in Fig. 3. The presence of boron in the treated samples can be further confirmed by XPS analysis in the boron region (Fig. 4), by the presence of the signal near 191.5 eV, which is associated to the B–O bond [29]. Moreover, as the amount of boron increases in the goethite particle, this signal is shifted to higher binding energies.

3.1.3. Mössbauer spectroscopy

Mössbauer transmission spectra at room temperature for the series of goethites are shown in Fig. 5(a) and the same hyperfine parameters obtained in this analysis are presented in Table 1.

The general forms of all spectra are similar; the difference between Gt-pure and the Gt-B samples (1 × 1 and 1 × 4) can be attributed to the higher magnetic field present in the pure sample. The Gt-pure spectrum can be considered as the superposition of two doublets formed by the central superparamagnetic relaxation of the oxide's characteristic sextet, related to small particle sizes. These small particles cause a fluctuation of the magnetic field, causing the observed superparamagnetic relaxation. The isomeric shift (δ) and quadrupole splitting values (Δ) for the Gt-B_{1 × 1} sample are similar, leading to a material mainly constituted by octahedral Fe(III), typical of a goethite-phase oxide.

For Gt-B_{1 × 4}, the results show that boron can interact with surface iron and cause some crystalline defects, when compared to the isomeric shift and splitting values for Gt-pure. The process of reduction of surface Fe(III) species destabilizes the goethite crystalline structure due to the excess of negative charges, this charge excess, in turn, causes a partial dihydroxylation, leading to point defects that can alter the valence and spin the compound's iron atoms [25]. These changes cause the increase in δ 0.37–0.39 mm s^{−1} and induce a local distortion (Δ) of 0.04–0.09 mm.s^{−1}, for Gt-pure and Gt-B_{1 × 4}, respectively. The Mössbauer spectroscopy sign with a lower Δ value can be attributed to Fe(III) octahedral sites, since largest Δ suggests iron in tetrahedral coordination [14]. The presence of iron in tetrahedral coordination agrees with the FTIR data for the presence of trigonal boron (BO^{3−}) vibrations and refraction and these data also suggests that there is a hybrid material composed of iron in magnetite and goethite phases. The Mössbauer spectrum profile consisting of a central doublet accompanied by a poorly defined sextet, along with the small particle size, refers to the presence of an iron phase different from goethite. Magnetically more ordered (magnetite), but which is not sufficient to change the hyperfine parameters for typical values of magnetite phase because the high concentration of typical goethite phase Fe(III) species within the material that could overlap the possible reduced iron species. Spectra were all fitted to the hyperfine field distributions shown in Fig. 5(b), reflecting a distribution of particle size or/and different degrees of boron incorporation. All samples present different average B_{hf} values at RT, and also differ from the B_{hf} value (38.2 T) reported for pure stoichiometric perfectly crystallized goethite [14]. The result showing that the boron present on the surface can interact with the surface iron and affected crystalline imperfections.

3.1.4. X-ray ABSORPTION NEAR EDGE STRUCTURE (XANES) SPECTROSCOPY

The above shown FTIR, XPS and Mössbauer characterization results were conclusive for the incorporation of boron on the surface of goethites, therefore, they were also inconclusive to the possible reduction of some Fe(III) species. Mössbauer spectroscopy, for example, would be a promising technique for analyzing this reduction, however, the Mössbauer data obtained by transmission were not analyzed with a surface approach. Thus, the high amount of Fe(III) species within the material can overlap possible reduced iron surface species. In this context, the materials were analyzed by spectroscopic XANES, an informative technique for the determination of oxidation states and local symmetry of transition metal ions. According to reference [30], the centroid position of the pre-edge strongly depends on the oxidation state of Fe, while its intensity is mainly influenced by its coordination geometry. Therefore, the presence of Fe(II) on the Fe(III) oxide can be easily addressed by measuring the centroid position on the normalized pre-edge peak.

Fig. 6 shows the typical iron K edge XANES spectra for the materials impregnated with boric acid. According to the spectrum of the precursor material whose iron phase is predominantly goethite phase (α -FeOOH), the XANES spectra (Fig. 6a), as well as other characterization techniques, show that the impregnated material has a similar nature to the precursor material whose absorption X-ray data confirms the formation of goethite phase. Furthermore, according to the data shown in Fig. 6b) by the increase in the pre-edge region of the spectrum, one can notice an increase in intensity and a slight shift to lower energy regions which is proportional to boron content. These spectral differences reflect the difference in the structural environments of Fe(II) and Fe(III). Thus, low intensity refers to a geometry with a center of symmetry, characteristic, for example, of octahedral layers. On the other hand, the increase in the intensity of the pre-edge when compared to the structure taken as standard (Gt-pure) reflects non-centrosymmetric geometries, distinctive for the tetrahedral coordination geometry. According to the data shown in Fig. 6b, it can be observed a variation in the intensity of the signals relating to the pre-edge energy of the material. When these signals are evaluated from the pure goethite in the direction of increasing boron content, an increase in intensity becomes evident. This increase is related to the formation of tetrahedral areas in a predominantly octahedral environment. This tetrahedral formation was evidenced by the hyperfine parameters shown in Table 1. Data indicates, therefore, the formation of a new iron phase mainly constituted by the octahedral coordinated metal and associated to the goethite phase joint to tetrahedral coordination, formed after treatment with and boron and derivatives, possibly magnetite phase (Fe₃O₄). Therefore, from the XANES data, it is possible to conclude that the treatment caused some modifications on iron's chemical environment, such as the possible reduction of some Fe(III) species.

4. Catalytic activity

4.1. Methylene blue degradation

The variation on the materials' catalytic activity for the methylene blue dye degradation reaction via Fenton process is shown in Fig. 7.

The results show that pure goethite has low activity in MB discoloration, with approximately 20% of discoloration after 240 min of reaction, while the boron-containing materials were more active. The effect of the modification with boron can be noticed to Gt-B_{1 × 1}, which led to 50% discoloration. Gt-B_{1 × 4}, in turn, showed an even more relevant efficiency for degradation of the compound. After

Table 1
Mössbauer spectra's hyperfine parameters.

Sample	Site ^{57}Fe	$\delta/\text{mm s}^{-1}$	$\Delta/\text{mm s}^{-1}$	Site
Gt-pure	Gt	0.37	0.04	$\text{Fe}^{3+}_{(\text{oct})}$
		0.42	−0.28	$\text{Fe}^{3+}_{(\text{oct})}$
Gt-B ₁ × 1	Gt	0.27	−0.03	$\text{Fe}^{3+}_{(\text{oct})}$
		0.37	0.08	$\text{Fe}^{3+}_{(\text{oct})}$
Gt-B ₁ × 4	Gt	0.32	−0.01	$\text{Fe}^{3+}_{(\text{oct})}$
		0.39	0.99	$\text{Fe}^{3+}_{(\text{tet})}$

Gt = Goethite; δ = isomeric offset relative to α -Fe, Δ = quadrupole splitting, tetrahedral = tet; octahedral = oct.

240 min of reaction, the material was able to degrade about 80% of the MB in the solution.

These results suggest that the modification with boron actually provides an easier electron transfer mechanism as evidenced by the increase in the oxidation rate, as one increases the proportion of boron in the materials. To corroborate the hypothesis of the effect of reduced sites on the efficiency of the catalysts, the greatest activity for the methylene blue reaction in the presence of hydrogen peroxide may be related to a kinetic favouring in the generation of oxygen radicals, provided by the system modified goethite/ H_2O_2 . The reaction in the absence of catalyst only with H_2O_2 , showed no significant discoloration of the dye solution by adsorption or uncatalyzed reaction. The discoloration of azo dyes is mainly through heterogeneous Fenton reaction, which depends on active sites in the specific area of the catalyst, the surface area of the catalyst was obtained by N_2 adsorption using the BET method. Gt-B₁ × 4 has a specific surface area of $68 \text{ m}^2 \text{ g}^{-1}$, Gt-B₁ × 1 has a specific surface area of $24 \text{ m}^2 \text{ g}^{-1}$ while pure has $17 \text{ m}^2 \text{ g}^{-1}$. The increasing the amount of boric acid added to the material accompanied by increased surface area, providing more active sites for the reaction. No adsorption effect was occurred due to specific surface area increase."

4.2. Methylene blue degradation products

The discoloration of the blue dye methylene solution proves that the activity of Gt-B₁ × 4 was increased. However, the total loss of color of methylene blue solution, after 240 min doesn't mean the organic compound was completely oxidized and gives little information about the involved reaction mechanism. Therefore, analysis by electrospray coupled to a mass spectrometer was performed for the points P1 and P2 indicated in Fig. 7 (Fig. 8).

For Gt-B₁ × 4 the formation of some organic intermediates were observed after 30 min of reaction, corresponding to the signals $m/z=270$ and 301 . The first signal was attributed to loss of one methyl group, and the second one is the first MB hydroxylation ($m/z=284 \text{ MB} + 17\text{HO}^*$), probably due to hydroxyl radicals formation and indicating a degradation via Fenton mechanism (Fig. 9). After 240 min of reaction, occurred the formation of intermediates with $m/z=276$, $m/z=247$ and $m/z=149$. The signal $m/z=276$ corresponding a hydroxylated and demethylated ion and the $m/z=247$ was formed due to over-oxidation of hydroxylated of intermediates. Finally, the signal of $m/z=149$ was indicative of the ring opening [31,32].

The increase in the oxidation rate is related to the presence of more active groups on the surface of goethite. The presence of these Fe(II) species provides a faster peroxide conversion compared to Fe(III) species [33,34]. Furthermore, the catalyst was used in sequential runs with a total of 15 cycles. The catalyst remained active after the successive cycles, indicating that the material was stable without change in the activity, discoloration around 90% after 15 cycles. Iron active species leaching was not observed. Furthermore, the material exhibits magnetic properties in response to a permanent magnet field (0.34 T), so that the catalyst can be recovered after degradation test.

In the literature, we found chemically reduced iron oxides prepared with sodium borohydride; however, catalytic tests for these materials have not yet been performed [18,35]. For boron-doped materials, we found results for photoactivated reactions [21] or Mn^{2+} adsorption [20]. For photodegradation of aniline by goethite doped with boron under ultraviolet and visible light irradiation, the half-lives ($t_{1/2}$) of aniline degraded by goethite and B-goethite under the ultraviolet light irradiation were 2.399 and 2.168 h respectively [21]. Our material, Gt-B₁ × 4 which, after 240 min of reaction, was able to degrade about 80% of the MB in solution, however without the presence of light. Munoz et al., 2015 [9] recently published a review of a material based on magnetite and its use in the heterogeneous Fenton like system. Considering the stability results for degradation of methylene blue, the material Gt-B₁ × 4 showed better results, with no loss of activity after 15 cycles, compared with those results presented in the review.

5. Potential energy curve: investigating the surface reactivity

In order to understand the surface of the material, theoretical calculations for the faces of pure and boron-modified goethites were performed. The chemical reaction between H_3BO_3 and the goethite structure occurs with the formation of one water molecule as shown in Fig. 10.

The theoretical results consider the interaction between H_3BO_3 with each face of goethite. In this context, the potential energy curve was evaluated from the bond length goethite-O \rightarrow B(OH)₃ in each 0.5 Å, whose values are shown in Fig. 11.

Results reported in Fig. 11 show the potential energy curve between the H_3BO_3 and the faces (001), (010), (011), (100), (101) and (110) of goethite. It should be kept in mind that for a chemical reaction to occur it is necessary that the reactants are able to both interact and form a transition state structure. In Fig. 11 the faces (001), (011) and (110) do not present the formation of any transition state structure, in other words, a chemical reaction between H_3BO_3 and goethite is not favourable. Turning now to faces (100), (010) and (110), it is possible to notice a formation of a transition state structure. However, a deeper analysis reveals that only the faces (010) and (110) are able to form a chemical intermediate with lower energy gap.

The charge density on pure goethite is also an important information, which can give insights on the material reactivity. Fig. 12 shows a great charge density around the oxygen atoms on the pure goethite's surface.

In fact, when H_3BO_3 was introduced close to (100) of goethite, a significant charge transfer between H_3BO_3 and the oxygen atoms from goethite-(100) takes place. In this process, the face 100 of goethite becomes more reactive. For instance, Fig. 12 shows the structure in periodic conditions between pure and boron-treated goethites at a 5.36 Å distance. From the presented theoretical findings, the treatment with the H_3BO_3 significantly modifies the electron density of goethite (100).

According to theoretical studies, the face (100) is more favourable for complexation of the acid and the

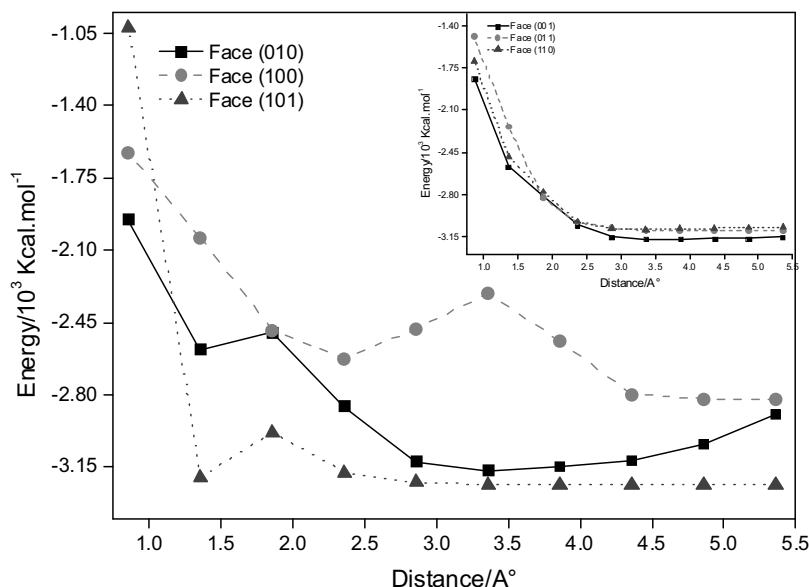


Fig. 11. Potential energy curves between H_3BO_3 and the goethite surface.

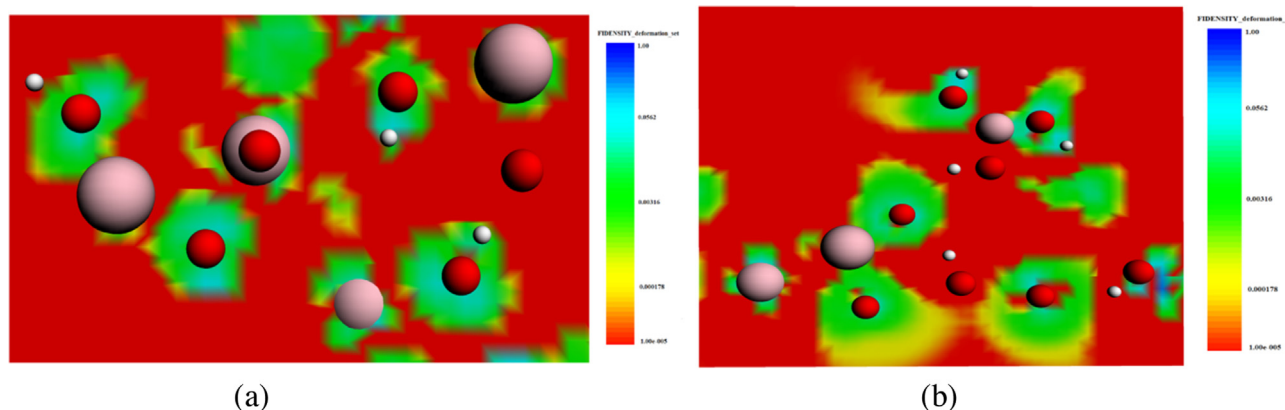


Fig. 12. Electron density contour area of the face 100 of goethite (a) pure goethite (b) treated with $\text{B}(\text{OH})_3$ at a distance of 5.36 Å.

goethite surface modification. According to Steele et al. for a synthetic goethite stability the order of faces is: (010) > (110) > (120) > (101) > (100) > (111) > (001), and the lower charge stability presented is explained by some incomplete connections on the iron atoms [37]. According to a study by reference [36], in a goethite, from a classical route, the face (100) is 50–60 percent of the total surface area of a sample.

6. Conclusions

The presence of boron in the oxide surface can be evaluated by theoretical studies and by the vibrations observed by FTIR, confirmed by the signal obtained by XPS, and the change of the Mössbauer hyperfine parameters. The presence of Fe(II) sites was identified by the shift and broadening of the XPS peaks, and also by the change in iron's chemical environment presented in the XANES spectra.

Pure goethite showed low capacity for methylene blue degradation when compared to the boron-modified materials. This behavior was related to the presence of Fe(III) in their structure, which presents H_2O_2 decomposition kinetics rather slow. The impregnation of boron in pure goethite caused a significant increase on the oxide's catalytic activity.

The presence of boron on the surface of the iron oxide facilitates the electron transfer process and causes the reduction of some Fe(III) to Fe(II) species, improving the system's kinetics and forming a greater number of oxidizing species, leading to the formation of reactive catalysts for Fenton chemistry. The study by mass spectrometry confirms that the mechanism of oxidation occurs *via* the Fenton system radical.

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